in the C-N-C angle in the pyridine ring occurs in all of the above cases. The changes in the bond angle may be rationalized in terms of an assumption of increased s character in the C-N bonds as predicted by Bent's rules.[17] The changes in the bond lengths appear to be more subtle and appear to depend on the nature of the group bonded to the nitrogen lone pair. However, these changes may account for the observed increased reactivity of pyridinium ions and related species.

Acknowledgment. We thank the NSF Instrumentation Program for a grant for the purchase of the Nicolet diffractometer.

Supplementary Material Available: Tables of the final thermal parameters, hydrogen atom parameters, and bond distances and angles (2 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

(17) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275-311.

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Hydrolysis Chemistry of the Chlorophosphazene Cyclic Trimer

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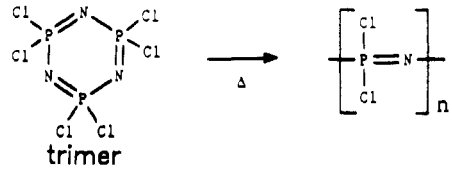
The hydrolysis chemistry of the chlorophosphazene (phosphonitrile chloride) cyclic trimer has long been of interest because of its possible relevance to polymerization catalysis, as well as the undesirable role of water in the cross-linking of poly(dichlorophosphazene). Hydrolysis of the trimer in THF solutions has been followed through the first 3 equiv of water by using ^{31}P NMR as the primary analytical tool. A total of seven products were identified, at least one of which has been previously proposed as a polymerization catalyst. Two of the species are oxo-bridged dimers of two trimer rings that may be useful as model compounds for hydrolytic cross-linking reactions in the polymer.

Introduction

The polymerization of the chlorophosphazene (phosponitrile chloride) cyclic trimer to form poly(dichlorophosphazene)

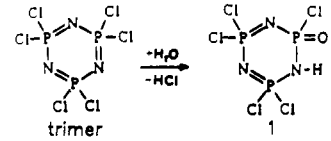


trimer

and subsequent derivatization leads to a large class of inorganic polymers with a wide range of properties. These properties include biocompatability, solvent resistance, thermal stability, and flame retardance.[1] Allcock and Best[2] proposed that the polymerization of trimer occurs via a ring opening cationic chain growth mechanism. The reaction can be performed either in the melt or in solution.

The melt polymerization reaction, typically carried out at temperatures between 180 and 220 °C, is extraordinarily sensitive to the presence of trace impurities that function as either catalysts, or inhibitors.[3] These effects are so extreme that the rate of polymerization varies profoundly from one batch of trimer to another or if two samples of trimer from the same batch are handled slightly differently. The role of water in the polymerization of trimer is very complex and poorly understood. Rigorously purified samples of trimer, obtained from multiple sublimations and recrystallizations, can require weeks to polymerize at 200 °C. Following exposure to atmospheric moisture, however, the polymerization rate is greatly accelerated. At low concentrations, water either acts as a polymerization catalyst or reacts with trimer to generate the active catalytic species. Indeed, Allcock and co-workers[3] have raised the question as to whether anhydrous samples of trimer could undergo melt polymerization at all. The eventual polymerization of highly purified trimer has been rationalized as the result of water or other contaminants leaching out of the glass reaction vessels.

One of the mechanisms proposed to explain the catalysis of polymerization is that water facilitates charge separation when a chloride ion dissociates from a trimer ring at elevated temperature. The resulting cation is then assumed to initiate polymerization.[3] Alternatively, Allcock and co-workers have proposed[3] that water catalyzes the polymerization indirectly by the formation of hydrolyzed trimer species (e.g., **1**), which are assumed



trimer 1

to ring open at elevated temperatures to form a charged initiator species. Identification of the products found early in the hydrolysis of trimer was one of the motivations of the present study.

Unfortunately, the role of water in the polymerization of trimer is not entirely favorable. At water contents greater than 1 mol %, an insoluble cross-linked polymer is formed, which can not be derivatized to form useful materials. The structure(s) of the cross-link sites are not known, but they can be expected to involve an oxo bridge between the chains. Hydrolytic cross-linking is somewhat unpredictable; therefore, it complicates the use of water as a polymerization catalyst. As Allcock[4] has pointed out, the chemistry of phosphazene polymers can frequently be modeled by carrying out analogous reactions on cyclic oligomers. A second motivation for the present study, therefore, was to investigate the possibility of hydrolytic cross-linking reactions (i.e., dimerization of cyclic trimeric units) when the trimer is exposed to water in solution. Such dimers, if formed, could presumably be used to model the cross-links formed by the action of water on poly(dichlorophosphazene).

Previous studies have focused on the later stages of hydrolysis, which ultimately lead to phosphoric acid and ammonium chloride. Those previous investigations employed chromatographic methods, which were complicated by further hydrolysis during the separation.[5] Because the putative catalytic species are usually envisioned as early products of the hydrolysis, we have used ^{31}P

* To whom correspondence should be addressed.

(1) Allcock, H. R. *Science* **1976**, *193*, 1214.
(2) Allcock, H. R.; Best, R. J. *Can. J. Chem.* **1964**, *42*, 447.
(3) Allcock, H. R.; Gardener, J. E.; Smeltz, K. M. *Macromolecules* **1975**, *8*, 36.
(4) Allcock, H. R. *Acc. Chem. Res.* **1979**, *10*, 351.
(5) (a) Pollard, F. H.; Nickless, G.; Warrender, R. W. *J. Chromatogr.* **1962**, *9*, 485. (b) Pollard, F. H.; Nickless, G.; Warrender, R. W. *J. Chromatogr.* **1962**, *9*, 493. (c) Quimby, O. T.; Narath, A.; Lohman, F. H. *J. Am. Chem. Soc.* **1960**, *82*, 1099.

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NMR spectroscopy to study the early stages of hydrolysis in solution. The results of this investigation clarifies the hydrolysis chemistry of trimer through the first 3 equiv of water. At least seven hydrolysis products were observed spectroscopically, several of them for the first time. Two of the compounds observed were oxo-bridged dimers of cyclic trimer units, which are proposed as models of the hydrolytic cross-link sites in the chloropolymer.

Experimental Section

All sample manipulation steps were performed in an inert atmosphere, either in a glovebox or with needles and septa to ensure that the only water entering the samples was that which was intentionally introduced.

Trimer was obtained from Aldrich (99.9+%) and Nipon Fine Chemicals (Phosnic 390). Regardless of source, samples of trimer were purified by recrystallization from hexane followed by three sublimations at 55 °C (10^{-2} Torr). The purity of trimer thus obtained was assured by confirming that melt polymerization at 200 °C did not commence for 4 weeks. Furthermore, ^{31}P NMR spectra of samples thus purified showed no signals other than that of trimer (+20.4 ppm), even after tens of thousands of scans.

Tetrahydrofuran (Fischer) was dried by distillation from sodium and benzophenone. Pyridine (Fischer) was dried over KOH and distilled from BaO. Hexane (Fischer) was dried by distillation from sodium, benzophenone, and diglyme. ^1H NMR was used to confirm the absence of water in all solvents. Triphenylphosphine oxide, (TPPO, Aldrich) was used as a quantification standard in some experiments, while $Cr(acac)_3$ (Aldrich), was used as a relaxation agent to permit shorter pulse delays in some experiments. Both were dried at 90 °C (10^{-2} Torr) and used without further purification.

NMR tubes (Wilmad, 10 mm) were cleaned with chromic acid and rinsed repeatedly with water followed by acetone. The tubes were then baked under vacuum at 200 °C prior to transfer to a glovebox. All ^{31}P NMR experiments were performed on a Varian XL-200 spectrometer operating at a resonance frequency of 81 MHz. ^{31}P NMR spectra were generally acquired by using a spectral width of 10000 Hz, and approximately 30K data points were taken to characterize the FID. Transients were acquired by using a 45° pulse and a recycle time of 1–11 s, depending on the need for quantification. In typical spectra, 32 scans provided excellent signal-to-noise ratios. The trimer (t) was used as a secondary internal chemical shift reference (+20.4 ppm relative to phosphoric acid). All ^{31}P chemical shifts are reported relative to phosphoric acid, and positive numbers denote downfield shifts. C_6D_6 (Aldrich, 99.5 %) was used as an internal lock. For those experiments requiring quantitative peak intensities, the proton decoupler was operated in a gated mode to prevent the build up of the nuclear Overhauser effect (NOE).

Approximately 30 hydrolysis experiments were monitored by ^{31}P NMR during the course of this investigation. Many of these experiments entailed spectral acquisition at periodic time intervals over the course of hours or days. Water loadings ranged from 0.5 equiv (on a Cl basis) to 20 equiv. All experiments were performed in either THF or THF/C_6D_6 solutions. In some experiments, pyridine (0.25–12 equiv) was added to probe the pH dependence of chemical shifts and coupling constants, as well as to investigate the hydrolysis chemistry of trimer under basic pH conditions. Selected experiments also employed a relaxation reagent ($Cr(acac)_3$) and a quantification standard (TPPO). Such experiments consisted of 0.75 g of trimer (0.022 mol), 0.20 g of TPPO (7.2×10^{-4} mol), 0.016 g of $Cr(acac)_3$ (4.6×10^{-5} mol), 3 mL of THF, and 1 mL of C_6D_6. NMR tubes were sealed with rubber septa so that water could be introduced immediately prior to spectral acquisition. In some cases, ^{31}P T_1 measurements, NOE measurements, and 2-D NMR experiments were performed in order to facilitate spectral assignment.

Mass spectral analysis was performed on a VG Analytical 70S high-resolution mass spectrometer equipped with a VG Analytical 11/250J data system. THF solutions of oxo-bridged dimers and other hydrolysis products were injected through the direct insertion port of that instrument.

Results and Discussion

Most of our experiments involved the addition of water to THF solutions of trimer without added acid or base, since this probably best models the conditions under which trimer samples encounter water contamination. Selected ^{31}P NMR spectra from a representative hydrolysis study of trimer are shown in Figure 1. Inspection of that figure reveals that the chemical shifts and coupling constants of some of the hydrolysis species display pronounced changes during the course of reaction. Such changes were principally due to variations in solution acidity during the reaction. Each hydrolysis step generates 1 mol of HCl, so the solution becomes progressively more acidic as hydrolysis proceeds. Many

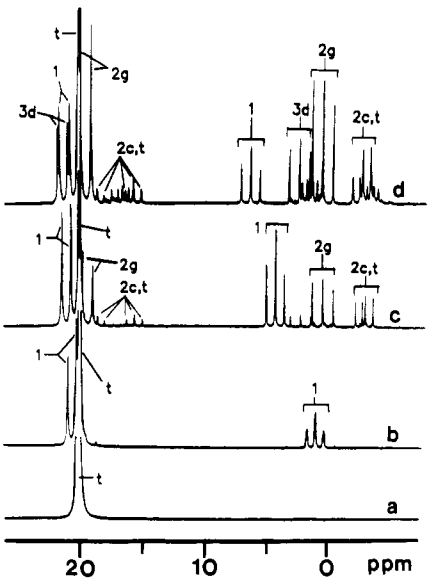


Figure 1. Selected ^{31}P NMR spectra from a representative hydrolysis study using 1 equiv of water. Spectra were acquired with an 11-s repitition delay, 45° pulse and 32 scans. Extent of reaction time: (a) 0 min; (b) 40 min; (c) 12 h; (d) 2 days. t = trimer; **2g = gem-2**; **2c,t** = *cis*-**2** and *trans*-**2**; **3d** = *dimer*-**3**.

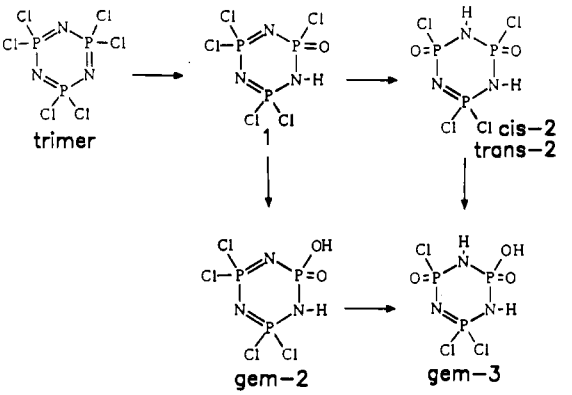


Figure 2. Reaction scheme for the hydrolysis of phosphazene chlorotrimer showing the monomeric products identified in this study.

of the signals also showed pronounced changes in shifts and/or couplings following addition of pyridine (vide infra), as well as smaller shifts following changes in solvent composition (e.g., addition of further aliquots of water). These variations in spectral parameters, combined with the complexity of the hydrolysis chemistry, made the unraveling of the hydrolysis pathway a moderately difficult exercise in spectral interpretation.

Several strategies were used to assign the ^{31}P spectra to specific products. In some cases, the spin-multiplicity patterns were uniquely characteristic of a particular species. One of the most useful strategies for assigning our spectra to specific hydrolysis products was to monitor the order of appearance of different signals; this strategy was particularly useful early in the hydrolysis when the number of species was relatively small. Finally, three of the observed hydrolysis products have been previously isolated as salts,[6-8] and some of their spectral properties were available in the literature (vide infra). These products provided benchmarks upon which other assignments could be anchored. Finally, mass spectrometry was used to support the assignments for the dimer species (vide infra).

The hydrolysis reaction scheme shown in Figure 2 was constructed from an analysis of several hundred ^{31}P NMR spectra

(6) Di Gregorio, F.; Marconi, W. *J. Org. Chem.* **1981**, *46*, 4569.
(7) de Ruiter, B.; Winter, H.; Wilting, T.; van de Grampel, J. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1027.
(8) Walsh, E. J.; Kaluzene, S.; Jubach, T. *J. Inorg. Nucl. Chem.* **1976**, *38*, 397.

Table I. ^{31}P NMR Spectroscopic Properties of the Hydrolysis Products of the Chlorophosphazene Cyclic Trimer (t)

product		^{31}P chem. shift (ppm)	$^2J(^{31}P-^{31}P)$, Hz	max NOE, %	T_1, s
trimer	PCl_2	20.4 (s)		4.8	14.7
1	PClO	7.3 (t)	59.5	60.9	10.9
	PCl_2	21.5 (d)		7.2	12.5
gem-**2**	PO_2	1.4 (t)	67.4	84.3	5.4
	PCl_2	19.9 (d)		13.9	9.5
cis-**2**	PClO	−1.4 (d)	44.3	64.2	6.8
	PCl_2	19.0 (t)		5.5	6.9
trans-**2**	PClO	−2.2 (d)	50.3	64.8	8.0
	PCl_2	16.2 (t)		8.5	7.4
gem-**3**	PO_2	2.4 (d, d)	28.3,68.0	82.4	4.3
	PClO	−2.7 (d, d)	28.3,42.4	61.0	4.5
	PCl_2	17.2 (d, d)	42.4,68.0	24.9	4.8
dimer-**3**	PO_2	3.2 (t)	65.5	78.5	11.0
	PCl_2	21.7 (d)			10.5
dimer-**1**	PClO	15.0 (t)	62.3		
	PCl_2	22.7 (d)			

taken over the course of numerous hydrolysis reactions. This scheme depicts all of the species that we have identified, with the exception of the oxo-bridged dimers, which will be described separately. The nomenclature used in Figure 2 is based on the number of moles of water consumed by a particular species. Compound **1** is formed when one molecule of water adds to the trimer to form a single product. Three products can be formed when **1** reacts with a second water molecule, all of which were observed. *gem*-**2** is the species formed when the second hydrolysis step occurs geminally to the first. Nongeminal hydrolysis leads to different products displaying cis–trans isomerism; these two products are designated *cis*-**2** and *trans*-**2**, respectively. It was not possible to unambiguously distinguish between the NMR signals of *cis*-**2** and *trans*-**2**; however, the assignments in Table I are consistent with the relative values of chemical shifts and coupling constants reported for salts of those compounds prepared by de Ruiter[7] (vide infra).

Further hydrolysis could be expected to lead to up to three possible monomeric isomers of **3**: *gem*-**3**, *cis*-**3**, and *trans*-**3**. Only *gem*-**3** was observed in our studies; it was identified unambiguously by its unique AMX splitting pattern. *cis*-**3** and *trans*-**3** have been previously proposed as hydrolysis products of trimer, and their salts have been prepared and isolated.[8] Our results suggest that geminal hydrolysis may be preferred, at least in the absence of a hindered base or sterically demanding counter ion.

Using larger additions of water (ca. 12 equiv or greater—corresponding to water concentrations of ca. 10 % or greater), it was possible to drive the hydrolysis reactions past 3 equiv of water before precipitation occurred. In such experiments, additional multiplet patterns were observed with chemical shifts and coupling constants as follows: 5.4 ppm, 14.7 Hz, (t); 3.8 ppm, 16.3 Hz, (t); −6.6 ppm, 16.1 Hz, (t); and −5.5 ppm, 10.1 Hz, (d). Although spectral overlap precluded resolution of some of the signals to which these multiplets were coupled and the samples were too reactive for 2-D experiments, these resonances are tentatively assigned to a trimer that has been hydrolyzed five times and the isomers of a trimer that has been hydrolyzed four times. No other assignable resonances were observed with further reaction, although additional hydrolysis was suggested by the formation of a large quantity of precipitate.

As stated previously, several of the hydrolysis products had ^{31}P chemical shifts and coupling constants that displayed a strong dependence on the acidity of the solvent; this was especially true for compound **1**. The PClO resonance of **1** first appears at a chemical shift of approximately 2.5 ppm when the trimer is subjected to hydrolysis in a water/THF solution. As the solution becomes more acidic from the formation of HCl, this resonance rapidly shifts downfield until it reaches a chemical shift of approximately 8.0 ppm. Similarly, the $^{31}P-^{31}P$ coupling constant is approximately 52.7 Hz at the first appearance of **1**, and this value changes to approximately 59.5 Hz under the more acidic

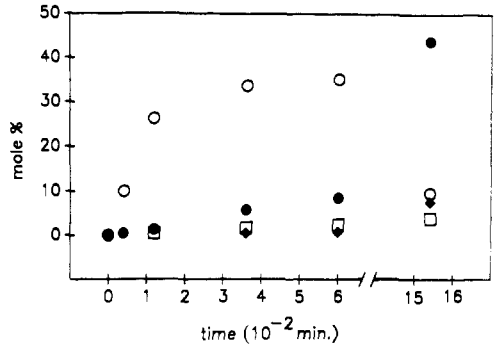
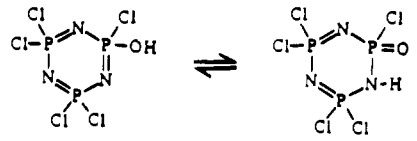


Figure 3. Mole fractions of various hydrolysis products vs time for a representative hydrolysis experiment (1 equiv of water). Dimer-**3** is seen to form after the monomeric species **1** and *gem*-**2**: (○) **1**; (●) *gem*-**2**; (□) *cis*-**2** and *trans*-**2**; (◆) dimer-**3**.

conditions prevailing later in the hydrolysis. Fortunately, the other NMR resonances observed in this study are not nearly so sensitive to acidity or solvent. The reason for the observed chemical shift changes probably involves the acid-base properties of the hydrolysis products and/or the position of the phosphazane–hydroxyphosphazene tautomeric equilibrium



(shown for **1**), which is generally viewed as favoring the phosphazane form.

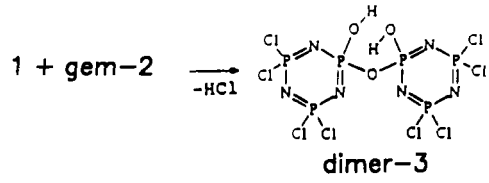
The dependence of the chemical shift of the PClO resonance of **1** on acidity can best be appreciated from an experiment in which the trimer was hydrolyzed by 0.5 equiv of water (on a Cl basis) in the presence of 0.25 equiv of pyridine. The chemical shift of this resonance remained constant around −0.8 ppm while the buffer capacity remained high. When the buffer capacity was exhausted, the chemical shift moved rapidly downfield to ca. +5.0 ppm. Several hydrolysis studies were carried out by using pyridine as a cosolvent, with the resulting chemistry being generally similar to that observed without added base (i.e. species **1**, **2g**, *cis*-**2**, *trans*-**2**, and *gem*-**3** were observed) except that the hydrolysis proceeded much faster. One additional product observed with added pyridine will be discussed later in this contribution.

Support for several of the assignments in Table I can be found in the literature. Di Gregorio and co-workers[6] have isolated the triethylammonium salt of **1** and reported its ^{31}P NMR spectrum in CH_2Cl_2. They observed a chemical shift of −1.93 ppm for the hydrolyzed phosphorous, a shift of +21.09 ppm for PCl_2 groups, and a coupling constant of 44 Hz. These values are in good agreement with those seen for **1** at the beginning of the pyridine experiment described earlier. de Ruiter and co-workers[7] reported the isolation of **1**, *cis*-**2**, and *trans*-**2** as salts of both $AsPh_4^+$ and $K(C_{12}H_{24}O_6)^+$. The ^{31}P chemical shift data reported in that study are also consistent with our data. Walsh and co-workers[8] reacted DMSO with trimer in acetonitrile to yield *cis*-**3** and *trans*-**3**; unfortunately, no ^{31}P NMR data were reported. These species would, however, yield distinctive splitting patterns, which were not observed in our study.

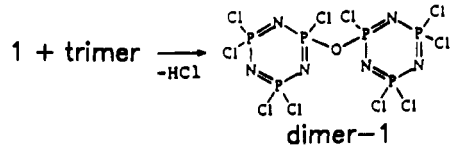
Dimer Formation. The spectra in Figure 1 show three products forming early in the hydrolysis which are characterized by an A_2X spin system with downfield doublets and upfield triplets: these are labeled **1**, *gem*-**2**, and dimer-**3** in the figure. The structures of **1** and *gem*-**2** are shown in Figure 2; however, it is difficult to imagine an additional monomeric hydrolysis product of trimer with NMR properties similar to those of **1** and *gem*-**2**. The solution to this problem was suggested by the work of Fedorov et al., who in 1984 showed[9] that an oxo-bridged dimer could be

(9) Fedorov, S. G.; Gol'din, G. S.; Kotova, E. V.; Kisin, A. V.; Nosova, V. M. *J. Gen. Chem. USSR (Engl. Transl.)* **1984**, *54*, 673.

formed from alkoxide-substituted trimer units. The possibility of dimer formation from the reaction of hydrolysis products with each other or trimer was therefore considered. Figure 3 shows a plot of mole fraction of hydrolysis product vs time from a reaction involving 1 equiv of water. The species labeled dimer-3 was not observed until both **1** and *gem*-**2** were present in significant concentrations, suggesting that those species are precursors to dimer-3. Species dimer-3 is assigned to the oxo-bridged dimer structure



A total of 3 mol of water are consumed in the production of 1 mol of dimer-3. Another dimer species could possibly form if **1** reacted with trimer



This species would also be characterized by an A_2X or A_2M spin system, and might be difficult to distinguish from species dimer-3 without further information. Fortunately, the triplet of dimer-3 is the only ^{31}P resonance observed in this study which exhibits a resolved coupling to protons (triplet pattern), $^2J(^1H-^{31}P) = 8$ Hz). This clearly rules out the possibility of confusing dimer-**1** and dimer-3. The triplet pattern is rationalized by assuming that strong intramolecular hydrogen bonding in dimer-3 minimizes intermolecular proton exchange while permitting an intramolecular exchange process which renders the protons equivalent.

When trimer is hydrolyzed in the presence of pyridine, however, an A_2M system is observed with a triplet centered at +15.0 ppm and a doublet centered at +22.7 ppm. This species forms after **1** has formed and cannot be confused with *gem*-**2** and dimer-3, which are also observed. These resonances are assigned to species dimer-**1**, which is proposed to form from **1** and trimer under base-catalyzed conditions. This reaction is somewhat analogous to the substitution reactions of trimer with alkoxides and aryloxides, which also occur under basic conditions. We have not observed the mixed dimer dimer-**2**. The reasons for this are unclear; either gem-**2** does not react with trimer, or dimer-**2** is too hydrolytically unstable to be observed in these experiments.

Supporting evidence for the existence of dimer species dimer-3 and dimer-**1** was obtained from mass spectrometric analysis of THF solutions immediately after NMR spectra revealed the presence of significant concentrations of the proposed dimer species. Mass spectra revealed the expected isotopic peak patterns for dimer-3 (centered about *m/e* 605) and dimer-**1** (centered about *m/e* 640). These patterns closely agreed with the calculated mass distributions for eight and ten chlorines, respectively, and can only be explained by dimeric species. Suitable control experiments showed that these peaks were only observed in solutions displaying the appropriate ^{31}P resonances. We propose that the formation of dimer-3 and dimer-**1** be used to model the hydrolytic cross-linking reactions of poly(dichlorophosphazene).

Trends in NMR Spectroscopic Parameters. Inspection of the data in Table I reveals several trends that are consistent with the proposed assignments. Protonation of the trimer ring as a result of hydrolysis reactions shortens the ^{31}P spin–lattice relaxation (T_1) times and results in an appreciable $^{31}P\{^1H\}$ NOE. If the phosphazane tautomers best describe the structures of the hydrolysis products, as assumed in Figure 2, hydrolysis will reduce the P–N bond order. This is reflected in a decrease in $^2J(^{31}P-^{31}P)$ values for extensively hydrolyzed products: e.g., 28.3 Hz for the coupling pathway in species *gem*-**3**, which has the lowest amount of π-bonding. As mentioned previously, several signals were observed that were probably due to species that had been more extensively hydrolyzed. These signals showed average coupling constants of ca. 14 Hz, suggesting a nearby complete disruption of π-bonding in the ring.

A close inspection of Table I reveals one chemical shift assignment that seems anomalous in comparison to the others: the bridging PClO groups of dimer-**1** have a chemical shift of 15 ppm—a value 8–18 ppm downfield from those of the other such groups in Table I. Species dimer-**1** is unique among the hydrolysis species observed in this study in that it is unable to adopt the phosphazane tautomeric form. The observed chemical shift is probably a good model for the hydroxyphosphazene tautomers of species such as **1**. If this view is correct, the downfield shift of the PClO resonance of **1** with increasing acidity suggests an increasing contribution from the hydroxyphosphazene tautomer in acidic solutions.

Conclusion

Spectroscopic identification of the hydrolysis products of trimer through addition of the first 3 equiv of water was achieved via ^{31}P NMR. At least one of the species observed has been previously proposed as a polymerization initiator. Further work in our laboratory is directed toward isolating several of the hydrolysis products for evaluation as polymerization initiators. Two oxo-bridged dimers were identified that may be used as model compounds for the hydrolytic cross-links which form upon exposure of the phosphazene chloropolymer to traces of water.

Acknowledgment. This work was supported by the Office of Naval Research (Grant N00014-88-K-0239). We wish to thank Dr. Tom Sharp of the Texas A&M University Mass Spectrometry Laboratory for his help in acquiring the mass spectral data.

(10) Paddock, N. L. *Q. Rev., Chem. Soc.* **1964**, *18*, 168.